New electrochromic mirror systems

Thomas J. Richardson*

Building Technologies Department, Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, MS62-203, Berkeley, CA 94720, USA

Abstract

Variable reflectance coatings (switchable mirrors) have significant advantages over traditional absorbing devices for radiant energy control in a variety of architectural and aerospace applications due to their large dynamic ranges in both transmission and reflection in the visible and near-infrared (NIR) regimes. Although electrochromic and gasochromic metal hydride films have been the primary focus of recent research in this field, other systems merit consideration. Two of these, based on electrochemical conversion of copper to copper oxides and of pnicogens to lithium pnictides are discussed here. Three distinct states are available in the copper system: the highly reflecting metal, the transparent Cu(I) oxide, and the black, highly absorbing Cu(II) oxide. Metallic thin films of elemental antimony and bismuth are reversibly converted to transparent, semiconducting lithium pnictides by cathodic polarization in a nonaqueous lithium electrolyte. Like the metal hydrides, these systems provide substantial modulation of near-infrared transmission and reflection, but have somewhat lower visible reflectance in their mirror states.
© 2003 Elsevier B.V. All rights reserved.

1. Introduction

Switchable mirrors based on hydrogen-induced phase transitions in rare earths [1] and mixtures of rare earth [2] or transition metals [3] with magnesium have attracted attention due to their numerous potential applications in solar heat control, communications, and display technologies. Switching may be achieved electrochemically or by exposure to hydrogen and oxygen gases. The highly reactive thin metal films are protected from oxidation by a thin layer of palladium, which also acts as a catalyst for introduction and removal of hydrogen. The low transparency of the Pd layer may limit the ultimate dynamic range of a device [4], and its ability to maintain an effective barrier toward air and corrosive electrolytes is unproven. A further obstacle to development of electrochromic hydride mirrors is the lack of a high-capacity optically passive counter electrode compatible with alkaline electrolytes.

Although the anodic formation of copper oxide films on bulk copper electrodes in alkaline electrolytes has been studied extensively [5,6], reversible electrochemical interconversion of copper and copper oxide thin films via solid state reactions was only recently demonstrated [7]. The initial film may be either the metal or an oxide, and any deposition technique that produces a uniform film may be used. The stability of the coating is highly pH-dependent.

* Tel.: +1-510-4868619; fax: +1-510-4868619.
E-mail address: tjrichardson@lbl.gov (T.J. Richardson).

Electrochromic oxide films operating via lithium ion insertion are well known [8]. Transparent counter electrodes and solid state, polymer, and gel electrolytes are well developed for devices of this type. The lithium-based electrochromic mirror awaits only an active electrode. Many metallic and semimetallic materials can be converted to semiconductors by addition or removal of lithium. The former class includes the present pnicogens, as well as silicon and germanium, tellurium, and even iodine. The latter include intercalated transition metal chalcogenides such as titanium disulfide [9] and niobium selenide [10].

The electrochemistries of the lithium–antimony and lithium–bismuth systems have been studied extensively by Huggins et al. [11–14]. While most of this work was carried out at elevated temperatures, where the formation of the metallic intermediates Li_2Sb and $LiBi$ are more easily distinguished, the interconversion of Sb and Bi to Li_3Sb and Li_3Bi are facile at room temperature. High lithium ion conductivities were observed in Li_3Sb and Li_3Bi, with considerable thermodynamic enhancement in the latter phase due to the existence of a range of stoichiometry between about $Li_{2.83}Bi$ and $Li_{3.05}Bi$. A much smaller stoichiometric range was found for Li_3Sb. Both compounds are known to be semiconductors, with a reported bandgap of 3.9 eV for Li_3Sb [15] and a calculated gap of 2.2 eV for Li_3Bi [16].

2. Experimental

Copper and copper oxide thin films were deposited on SnO_2:F-coated glass substrates by DC magnetron sputtering as described in Ref. [7]. Electrochemical cycling was carried out in 0.1 M NaOH using a Pt counter electrode and HgO/Hg reference electrode. Antimony and bismuth films were prepared on glass substrates by evaporation of the metals in a vacuum coater. Film thicknesses were measured by profilometry (Dektak). Electrochemical cycling was carried out in a 50-ml fused silica cuvette containing 1 M $LiClO_4$ in propylene carbonate, using lithium foil counter and reference electrodes. Photopic transmittance was monitored in situ using a filtered silicon detector (International Light) with output coupled to a computerized potentiostat/galvanostat (Arbin). Visible spectra were recorded using a fiber optic spectrometer (Ocean

Optics). X-ray diffraction (XRD) patterns of films as deposited and after cycling were obtained using a Siemens thin film diffractometer with an incident beam angle of 0.5° from the sample surface.

3. Results and discussion

The oxidation of a copper film to Cu_2O in 0.1 M NaOH proceeds in three distinct steps between − 0.4 and 0.2 V vs. HgO/Hg. Beginning at a slightly higher potential, Cu_2O is oxidized to the structurally similar CuO. Although the latter is a good electronic conductor, the mobility of oxide ions in CuO is poor relative to that in Cu_2O due to the filling of oxide vacancies. Once a surface layer of CuO is formed, the further oxidation of Cu_2O is thwarted, even above 0.7 V, when oxygen evolution from the CuO surface is rapid, thus limiting the switching range between transparent Cu_2O and black CuO. Transmittance and reflectance spectra between 400 and 1000 nm for a 25-nm Cu film before and after conversion to Cu_2O (20th cycle) are shown in Fig. 1. The dashed line is the total reflectance spectrum of an optically dense Cu film. Note that in transmission, the 25-nm metallic film has a slight blue-green color due to the window at 560 nm. The visible transmission varies by as much as 50% between states, with a similar modulation of reflectance in the near-infrared (NIR).
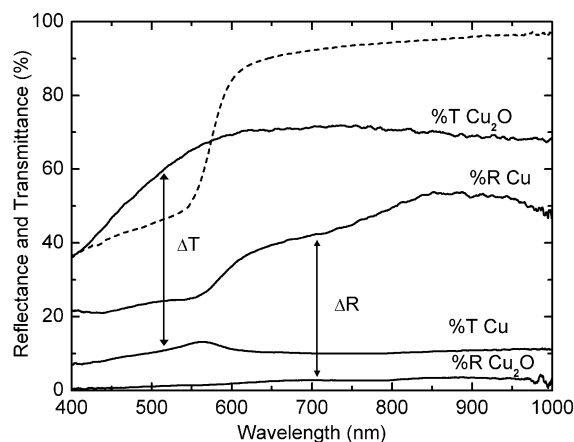

Fig. 1. Transmittance (*T*) and reflectance (*R*) switching behavior as a function of wavelength for a 25-nm-thick Cu film on SnO_2:F-coated glass in 0.1 M NaOH. The dashed line shows the reflectance spectrum of an optically dense Cu film.

The potential of a fresh antimony film is about 2.5 V vs. Li due to the presence of a small amount of oxide. As lithium is taken up, the potential drops rapidly to a plateau at about 0.8 V (Fig. 2). Transparent conducting oxide coatings are not used as they are not stable at these potentials. The current is carried entirely by the antimony film. Because the formation potentials of Li_2Sb and Li_3Sb are very similar [14], only the latter is observed during lithiation. Near the end of lithiation, the drop in potential is gradual due to migration of lithium into the portion of the film, which is not wetted by the electrolyte. This also results in a slower bleaching of the film in this region, and a larger discharge capacity. The lithium is removed at about 1.1 V, showing that Li_3Sb retains sufficient conductivity to facilitate the reversion to the metal phase, and that the metallic and semiconducting portions of the film maintain contact despite the thickness change during cycling. The charge passed on oxidation of the film corresponds closely to three electrons per Sb atom in the wetted portion of the film. The changes in the visible-NIR transmission spectrum (Fig. 3) also suggest formation of the transparent Li_3Sb throughout the bleaching process, rather than formation of a metallic intermediate. Repeated cycling between the metallic and transparent states resulted in gradual coarsening of the Sb grains, a lessened specular appearance in the metallic state, and a slow deterioration in the dynamic range, while the reversible capacity remained constant.
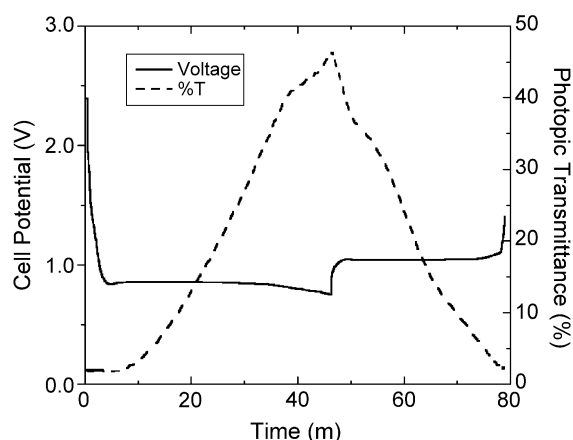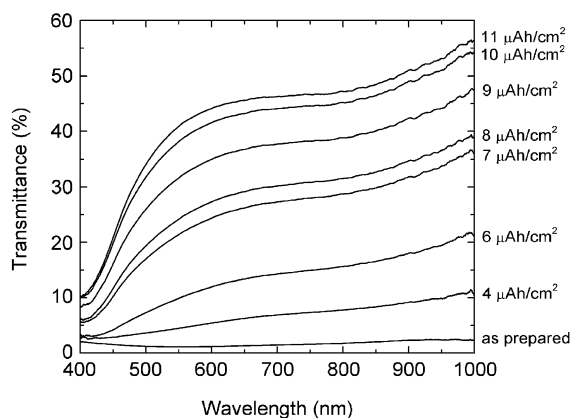

Fig. 3. Visible-NIR transmission spectrum of a 25-nm-thick Sb film during lithium insertion.

The behavior of bismuth is quite similar to that of antimony, except that after the pale yellow state is achieved, further insertion of lithium results in a strong electrochromism within the transparent phase, with a dramatic red shift in the absorption edge for small increments of excess lithium (Fig. 4). The precise composition was not established, but the range of excess lithium beyond the state of maximum transparency is about 0.1 per Bi atom. Switching in this range was very stable, with no deterioration over hundreds of cycles.
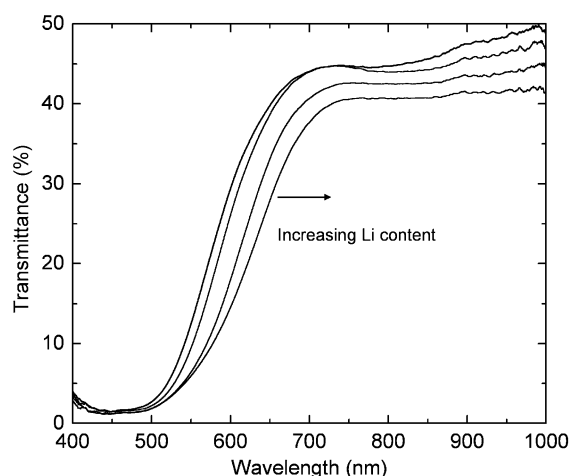

Fig. 2. Cell potential and photopic transmittance vs. time for a 25-nm-thick Sb film during lithium insertion and extraction. Current density: 20 $\mu A/cm^2$.

Fig. 4. Shifting of the absorption edge with excess lithium in a 30-nm-thick $Li_{-3}Bi$ film.

4. Conclusions

Metallic copper exhibits very high near-infrared reflectance, but is much less reflecting below about 600 nm. Cu_2O has low reflectance in both the visible and near-IR. These characteristics make the copper–copper(I) oxide couple attractive for use in architectural applications where high visible reflectance may be undesirable, but where strong reflectance and transmittance modulation of infrared light could lead to significant energy savings.

Metallic thin films of elemental antimony and bismuth, deposited on glass substrates by vacuum evaporation, are reversibly converted to transparent, semiconducting lithium pnictides by cathodic polarization in a nonaqueous lithium electrolyte. Dramatic changes in transmission and reflection accompany the phase transitions, which are reversible and can be used as the basis of a switchable mirror system. The estimated optical bandgaps of the yellow semiconducting phases Li_3Sb and Li_3Bi are about 3.1 and 3.5 eV, respectively. Varying the lithium content in a narrow region of nonstoichiometry in $Li_{3 \pm x}Bi$ produces a reversible color change from yellow $Li_{\sim 3}Bi$ to red $Li_{\sim 3.1}Bi$ due to a shift in the absorption edge, which results in modulation of the photopic (visible) transmittance by a factor of 3 for a film with an initial thickness of 25 nm.

Switchable mirrors can be made from a variety of materials with unique properties and chemistries. The systems described here are based on metallic hosts that are stable with respect to the electrolytes and can be recovered without irreversible losses of active material. The large volume changes that take place during cycling result in physical modification of the host particles. It may be possible to mitigate the effects on electrode performance through device engineering. Alternatively, new systems with smaller volume changes may become available.

References

[1] J.N. Huiberts, R. Griessen, J.H. Rector, R.J. Wijngaarden, J.P. Dekker, D.G. de Groot, N.J. Koeman, Nature (Lond.) 380 (1996) 231.
[2] P. van der Sluis, M. Ouwerkerk, P.A. Duine, Appl. Phys. Lett. 70 (1997) 3356.
[3] T.J. Richardson, J.L. Slack, B. Farangis, M.D. Rubin, Appl. Phys. Lett. 80 (2002) 1349.
[4] K. von Rottkay, M. Rubin, P.A. Duine, J. Appl. Phys. 85 (1999) 408.
[5] H.Y.H. Chan, C.G. Takoudis, M.J. Weaver, J. Phys. Chem., B 103 (1999) 357.
[6] S. Hartinger, B. Pettinger, K. Doblhofer, J. Electroanal. Chem. 397 (1995) 335.
[7] T.J. Richardson, J.L. Slack, M.D. Rubin, Electrochim. Acta 46 (2001) 2281.
[8] C.G. Granqvist, Handbook of Inorganic Electrochromic Materials, Elsevier, Amsterdam, 1995.
[9] A.R. Beal, S. Nulsen, Philos. Mag., B 43 (1981) 965.
[10] J.V. Acrivos, C. Delios, N.Y. Topsoe, J.R. Salem, J. Phys. C 3 (1971) L18.
[11] W. Weppner, R.A. Huggins, J. Electrochem. Soc. 124 (1977) 1569.
[12] W. Weppner, R.A. Huggins, J. Solid State Chem. 22 (1977) 297.
[13] W. Weppner, R.A. Huggins, J. Electrochem. Soc. 125 (1978) 7.
[14] J. Wang, I.D. Raistrick, R.A. Huggins, J. Electrochem. Soc. 133 (1986) 457.
[15] R. Gobrecht, Phys. Status Solidi 13 (1966) 429.
[16] M. Tegze, J. Hafner, J. Phys., Condens. Matter 4 (1992) 2449.